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Review

Study of Mg–Al–Ca magnesium alloy ameliorated with designed $\text{Al}_8\text{Mn}_4\text{Gd}$ phase

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Abstract

To investigate the effect of $\text{Al}_8\text{Mn}_4\text{Gd}$ phase on microstructural and mechanical properties of Mg–Al–Ca magnesium alloy, two Mg–2.5Al₂Ca and Mg–2.5Al₂Ca–0.1Al₈Mn₄Gd alloys were designed and compared in this work. The results show that a small amount of Gd can significantly refine α -Mg grains and change the morphology of Al₂Ca particles. Indeed, the formed $\text{Al}_8\text{Mn}_4\text{Gd}$ phase could serve as a heterogeneous nucleation site for the α -Mg grains and Al₂Ca particles. Furthermore, the introduction of Gd not only optimized the mechanical properties of Mg–Al–Ca alloy, but also facilitated the thermal deformation (such as hot rolling).

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Keywords: Mg–Al–Ca alloy; $\text{Al}_8\text{Mn}_4\text{Gd}$ phase; Microstructure and mechanical properties; Hot rolling.

1. Introduction

Magnesium alloy castings have a great advantage in vehicle light-weighting, and aerospace engineering due to the low density, short processing cycle and assembly costs, which have attracted numerous studies [1–8]. As AZ series of magnesium alloy exhibits soften behavior at elevated temperature, Mg–Al–Ca alloys was developed to evaluate the mechanical properties due to the low price, texture weakening and good ignition resistance [9–11]. However, the poor plastic deformation ability and mechanical properties of as-cast Mg–Al–Ca alloys are challenges still to be addressed yet.

In cast Mg–Al–Ca alloys, the typical microstructure contains two phases: α -Mg grains and β -Al₂Ca [12]. Consequently, the most effective way to improve mechanical properties of Mg–Al–Ca based alloy is to modify β -Al₂Ca by alloying with Mn, Zn, Si, Sr and Rare Earth (RE) elements,

etc. [13–16]. The modification mechanism is that the new formed particles could provide the nucleation site for the second phase. To fulfill this step, the particle should firstly form and exhibit one good crystallographic match with the second phase during solidification. For example, Li et al. [17] reported that introduction of manganese (Mn) into the as-cast Mg–5.5Al–3Ca wt.% alloys resulted in the formation of Al_8Mn_5 phase and increased the yield strength of the alloy from 366 MPa to 402 MPa. However, Mn addition has no refining effect on the microstructure of the as-cast alloys. Nakata et al. [18] reported that only 1% of Zn addition could significantly improve both strength and ductility of rolled Mg–8Al–1Ca–0.3Mn (AX81) alloy sheet. This is because that introduction of Zn facilitated the formation of homogeneous grain structure and isotropic basal texture. Son et al. [19] found that samarium (Sm) addition resulted in a microstructure composed of equiaxed and refined grains and grain sizes in Mg–5 wt%Al–3 wt% Ca-based alloys.

Recently, Li et al. [20] found that the formation of $\text{Al}_8\text{Mn}_4\text{Gd}$ phase in AZ91 alloy could significantly refine

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Table 1
Nominal composition of experimental alloys (wt.%).

Experimental alloys	Mg	Al	Mn	Ca	Gd
Mg-2.5Al ₂ Ca-0Al ₈ Mn ₄ Gd	90.533	5.433		4.035	
Mg-2.5Al ₂ Ca-0.1Al ₈ Mn ₄ Gd	88.276	6.232	0.875	3.99	0.626

α -Mg grains and Mg₁₇Al₁₂ particles, as Al₈Mn₄Gd phase can act as the heterogeneous nucleation site. However, so far, there are few reports about the effect of Al₈Mn₄Gd phase in Mg–Al–Ca alloy. Therefore, in the present work, two Mg–2.5Al₂Ca and Mg–2.5Al₂Ca–0.1Al₈Mn₄Gd alloys were designed and compared for investigating the effect of Al₈Mn₄Gd phase on microstructural and mechanical properties of Mg–Al–Ca magnesium alloy.

2. Experimental procedure

The mold and all tools of gravity casting were firstly pre-heated up to 250 °C for removing the moisture. The electric resistance furnace was used to melt 1 kg pure Mg and Al together in a steel crucible protected under the protection a mixture gas of CO₂ and SF₆, pure Mg and Al were heated to be melt in one electric resistance furnace. Subsequently, MgGd₃₀ and MgMn was used as master alloys for introducing Gd and Mn element. Then Ca was introduced through CaAl₂₀ master alloys. The melt was continuously held and stirred at 720 °C for 20 min after complete melting, homogeneous melt Mg–2.5Al₂Ca–0.1Al₈Mn₄Gd alloy was finally obtained and was poured into a pre-heated steel mold at 250 °C. The nominal composition of experimental alloys was given in Table 1.

Samples for observation were ground with silicon carbide and then successively polished with 6 μ m, 3 μ m, 1 μ m and 0.25 μ m diamond suspensions. To avoid the work-hardening caused by conventional grinding, a chemo-mechanical polishing was performed using Al₂O₃ (particle size: 0.04 μ m) suspension. A diluted acetic acid solution comprising 50 mL distilled water, 150 mL anhydrous ethyl alcohol and 1 mL glacial acetic acid was used to etch the specimen surface. Scanning Electron Microscope (SEM) observation (Zeiss Merlin Germany) and X-Ray Diffraction (XRD) using Bruker D8 diffractometer (Karlsruhe, Germany) with Cu-K α radiation were adopted to perform the microstructural observation and phase identification.

Tensile test was performed on a universal servo-hydraulic mechanical testing machine (Instron 5600, Norwood, MA) equipped with a knife-edge extensometer with a strain rate of 1 mm/min at room temperature in air. The samples were fabricated following GB/T228.1–2010 flat specimen standard. The dimensions were 85 mm in overall length and 35 mm in gauge length, 25 mm width and 15 mm in thickness. Each test was repeated six times for each composite in order to evaluate the corresponding mechanical properties.

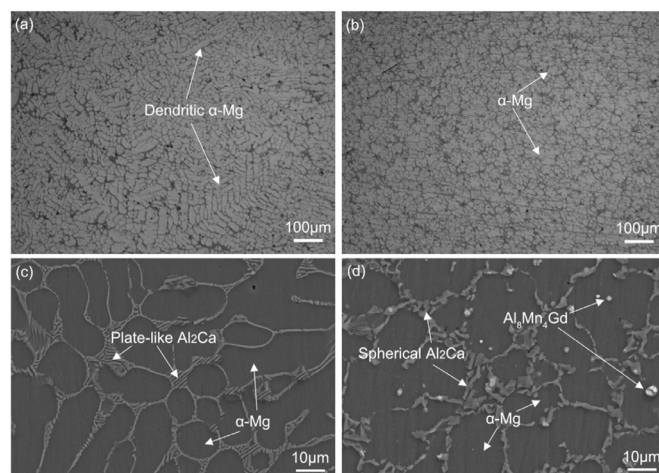


Fig. 1. Optical (top) and SEM (below) Morphologies of as-cast MgAlCa-0Gd (left) and Mg–Al–Ca–0.1Gd (right) alloys.

3. Results

3.1. Microstructural morphology and refine mechanism

The morphology and distribution of the particles in as-cast alloys were respectively observed by optical and SEM micrographs, as shown in Fig. 1, it is clear that Mg–Al–Ca alloy exhibit typical dendritic structure. (Fig. 1a). A lot of gray plate particles (Al₂Ca phase confirmed in Fig. 2) are found around the α -Mg dendrites and in α -Mg inter-dendrites (Fig. 1c). When Gd was added into Mg–Al–Ca alloy, the dendritic degree of α -Mg strongly decreased (Fig. 1b). Fig. 1d shows that the plate-like Al₂Ca changed into the spherical form and a new phase Al₈Mn₄Gd formed. It is confirmed by XRD shown in Fig. 2a.

As found from XRD result given in Fig. 2a, only α -Mg and Al₂Ca two phases were detected in Mg–Al–Ca alloy, while the new phase Al₈Mn₄Gd appeared when Gd was introduced into Mg–Al–Ca alloy. In addition, Fig. 2b shows the solidification paths of as-cast Mg–4Al₂Ca and Mg–0.5Al₈Mn₄Gd alloys calculated by Scheil model. It reveals that the Al₈Mn₄Gd phase precipitated at the temperature of 640 °C during the solidification process, while the precipitation of α -Mg and Al₂Ca phase starts below 600 °C.

As Al₈Mn₄Gd phase precipitated earlier than α -Mg and Al₂Ca phases, its ability of acting as potent nucleation sites for the α -Mg grains and Al₂Ca could be calculated by Bramfitt's equation shown in Eq. (1) [21], the degree of potency of the nucleation catalysts based on the average disregistry along low-index directions within low-index planes between

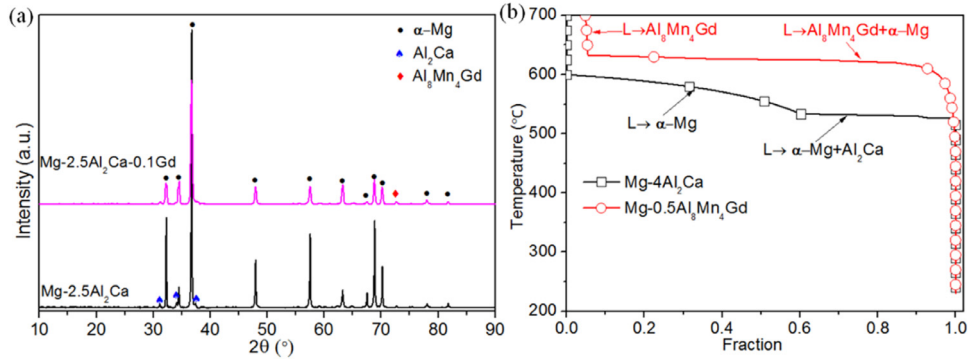


Fig. 2. (a) XRD patterns of as-cast MgAlCa-0Gd and MgAlCa-0.1Gd alloys (b) the solidification route calculated of Mg-4Al₂Ca and Mg-0.5Al₈Mn₄Gd alloys by JMatPro.

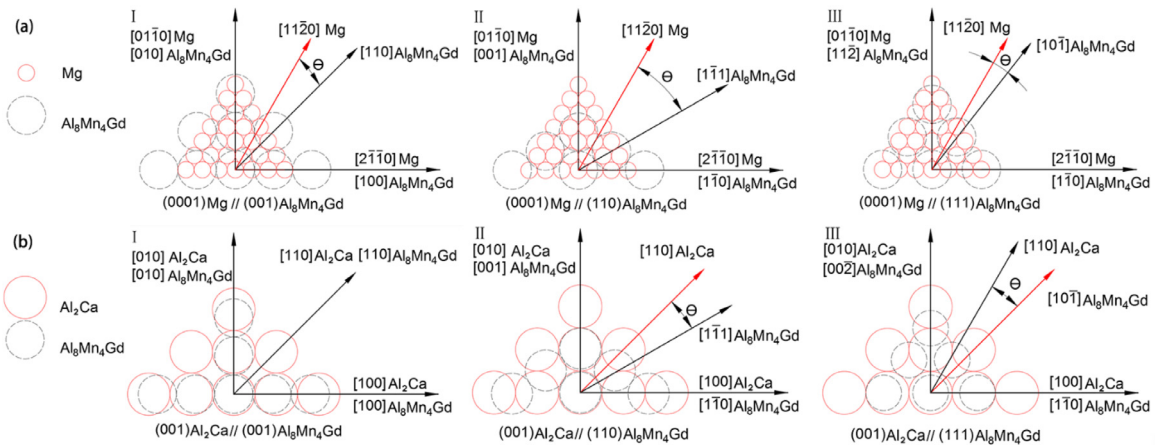


Fig. 3. Schematic plans of the crystallographic relationships:(a) between Mg and Al₈Mn₄Gd. (b) between Al₂Ca and Al₈Mn₄Gd.

substrate and nucleation solid.

$$\delta_{(hkl)_n}^{(hkl)_s} = \sum_i^3 \left[\left(|d_{[uvw]_s^i} \cos \theta - d_{[uvw]_n^i}| / d_{[uvw]_n^i} \right) / 3 \right] \times 100\% \quad (1)$$

Where (hkl)_s is a low-index plane of substrate, [uvw]_s is the low index direction in (hkl)_s, d_{[uvw]_s} is the interatomic spacing along [uvw]_s, (hkl)_n is a low-index plane in the nucleation solid, [uvw]_n is the low-index direction in (hkl)_n, d_{[uvw]_n} is the interatomic spacing along [uvw]_n, and θ is the angle between [uvw]_s and [uvw]_n. If the disregistry δ of lattice spacing is less than 15%, the substrate can promote the nucleation of melt material. Mg is hexagonal structure with the lattice parameters of a = 0.32093 nm and c = 0.52103 nm. Al₈Mn₄Gd is tetragonal structure with the lattice parameters of a = 0.8929 nm and c = 0.512 nm. Al₂Ca is cubic structure with the lattice parameters of a = 0.802 nm.

Three low-index planes of Al₈Mn₄Gd, including (100), (110) and (111) were selected as matching planes. The (0001) plane of Mg and the (001) plane of Al₂Ca were used as nucleating plane. The schematic plans of the crystallographic relationships between Mg and Al₈Mn₄Gd, Al₂Ca and Al₈Mn₄Gd were shown in Fig. 3. By using the lattice parameters and Eq. (1), the disregistry between Mg and Al₈Mn₄Gd, Al₂Ca

and Al₈Mn₄Gd were calculated and summarized in Tables 2 and 3. It was found that the mismatch was just 7% between [1-10] direction on the (111) plane of Al₈Mn₄Gd and [2-1-10] direction on the (0001) plane of Mg. Thus, Al₈Mn₄Gd can act as nucleation site to refine the α-Mg grains, which was also reported during the alloy solidification process [22–25]. Between Al₂Ca and Al₈Mn₄Gd, the calculation indicates that the mismatch was 0.113 (below 0.15) when the (110) plane of the Al₈Mn₄Gd was overlapped on the (001) plane of the Al₂Ca. Thus, the refining effect of Al₈Mn₄Gd on Al₂Ca as nucleation site is useful but not effective. This was consistent with the results shown in Fig. 1, the size of Al₂Ca phase only became a slightly smaller with the formation of Al₈Mn₄Gd phase. Moreover, the Al₂Ca lamellar located at the grain boundaries evolved into granular from with the formation of Al₈Mn₄Gd phase in Mg–Al–Ca alloy. Therefore, we confirmed that formation of Al₈Mn₄Gd phase could lead to efficiently refine α-Mg and change Al₂Ca phase morphologies, but the Al₂Ca phase was slightly refined.

3.2. Mechanical properties of as-cast and hot rolled

The room temperature stress-strain curves of the as-cast alloys and hot rolled ones are presented in Fig. 4. For the as-cast specimens, the addition of Gd into Mg-

Table 2
The results of planar disregistries between Mg and Al₈Mn₄Gd.

α -Mg plane	Al ₈ Mn ₄ Gd plane	α -Mg orientation	Al ₈ Mn ₄ Gd orientation	Results	Average
(0001)	(001)	[2 $\bar{1}$ 10]	[100]	0.22	0.27
		[11 $\bar{2}$ 0]	[110]	0.20	
		[01 $\bar{1}$ 0]	[010]	0.39	
(0001)	(110)	[2 $\bar{1}$ 10]	[1 $\bar{1}$ 0]	0.07	0.16
		[11 $\bar{2}$ 0]	[1 $\bar{1}$ 1]	0.32	
		[01 $\bar{1}$ 0]	[001]	0.08	
(0001)	(111)	[2 $\bar{1}$ 10]	[1 $\bar{1}$ 0]	0.07	0.11
		[11 $\bar{2}$ 0]	[10 $\bar{1}$]	0.18	
		[01 $\bar{1}$ 0]	[11 $\bar{2}$]	0.08	

Table 3
The results of planar disregistries between Al₂Ca and Al₈Mn₄Gd.

Al ₂ Ca plane	Al ₈ Mn ₄ Gd plane	Al ₂ Ca orientation	Al ₈ Mn ₄ Gd orientation	Results	Average
(001)	(001)	[100]	[100]	0.113	0.11
		[110]	[110]	0.113	
		[010]	[010]	0.113	
(001)	(110)	[100]	[1 $\bar{1}$ 0]	0.575	0.319
		[110]	[1 $\bar{1}$ 1]	0.107	
		[010]	[001]	0.277	
(001)	(111)	[100]	[1 $\bar{1}$ 0]	0.575	0.229
		[110]	[10 $\bar{1}$]	0.10	
		[010]	[11 $\bar{2}$]	0.014	

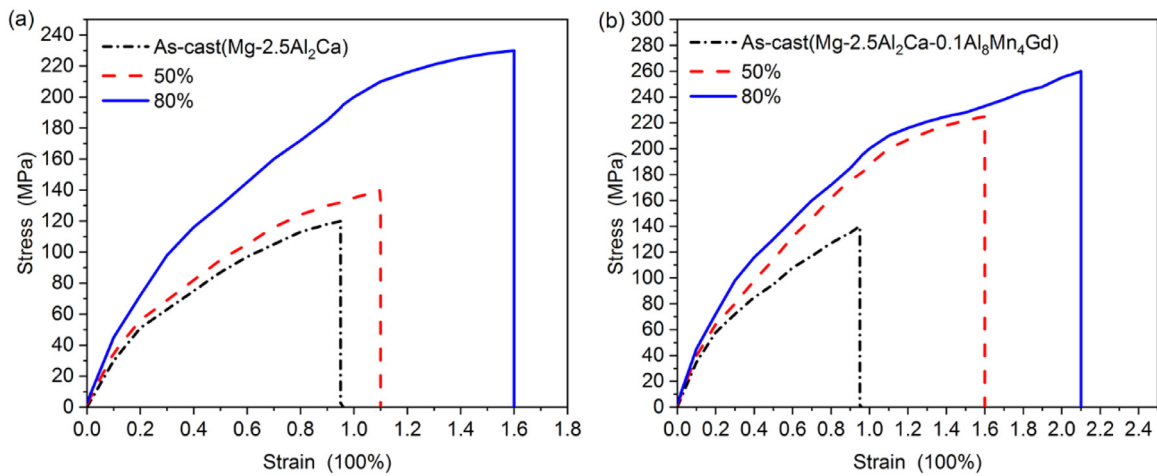


Fig. 4. Tensile stress-strain curve of as-cast and hot rolled specimens (a) Mg-2.5Al₂Ca alloy and (b) Mg-2.5Al₂Ca-0.1Al₈Mn₄Gd alloy.

2.5Al₂Ca alloy only has one weak improvement on the tensile strength and ductility. However, Mg-2.5Al₂Ca and Mg-2.5Al₂Ca-0.1Al₈Mn₄Gd alloys exhibit obvious different improvement in mechanical properties with hot rolling deformation. With 50% hot-roll deformation degree, the Ultimate Tensile Strength (UTS) and ductility of as-cast Mg-2.5Al₂Ca-0.1Al₈Mn₄Gd alloy were remarkably enhanced from 140MPa and 1.1% to be 225MPa and 1.6%. With further deformation to be 80% degree, UTS and ductility of Mg-2.5Al₂Ca-0.1Al₈Mn₄Gd alloy could reach 260MPa and 2.1%. In contrast, the UTS and strain of Mg-2.5Al₂Ca were only enhanced from 119MPa and 0.95% to be 140MPa and 1.1% with 50% hot-roll deformation degree. Subsequently, different from the continuous improvement found in hot rolled 2.5Al₂Ca-0.1Al₈Mn₄Gd alloy, the UTS and strain of Mg-2.5Al₂Ca alloy

suddenly jumped to 230MPa and 1.6% with 80% deformation degree, even though these values are still lower than those of deformed Mg-2.5Al₂Ca-0.1Al₈Mn₄Gd.

Fig. 5 presents the microstructural morphologies of hot rolled two alloys with different degree of hot rolling deformation treatment. It is evident that both two alloys exhibit different Al₂Ca distribution. Even after hot rolling with 50% deformation degree, the lamellar Al₂Ca phase still accumulated with one necklace form in Mg-2.5Al₂Ca alloy. In contrast, Al₂Ca and Al₈Mn₄Gd phases already uniformly dispersed in Mg-2.5Al₂Ca-0.1Al₈Mn₄Gd alloy. When the deformation degree of specimens reached 80%, the lamellar Al₂Ca phase was almost broken and well distributed in Mg-2.5Al₂Ca alloy. Herein, one jump in mechanical properties occurred in hot rolled Mg-2.5Al₂Ca alloy from 50% to 80% deforma-

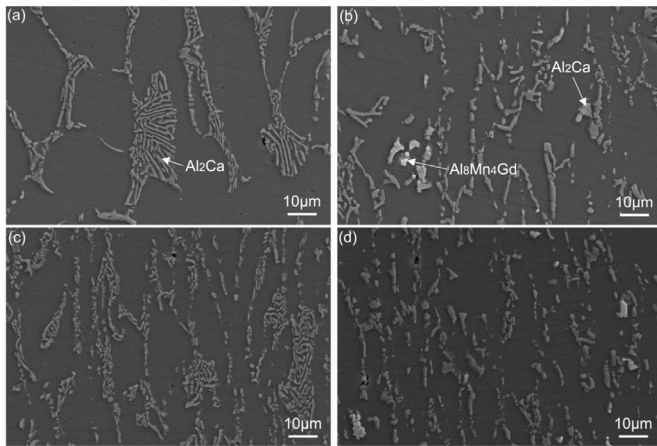


Fig. 5. The SEM morphologies of as-cast Mg-2.5Al₂Ca and Mg-2.5Al₂Ca-0.1Al₈Mn₄Gd alloys with different degree of hot rolling deformation treatment: (a and b) 50% and (c and d) 80%.

tion degree. At the same time, the distribution of Al₂Ca and Al₈Mn₄Gd particles become more uniform in Mg-2.5Al₂Ca-0.1Al₈Mn₄Gd alloy.

Fig. 6a and b show the tensile fracture of two as-cast alloys. The α -Mg dendrite form was found in tensile fracture of as-cast MgAlCa-0Gd alloy, the fracture surface was mainly occupied by cleavage surfaces. However, no α -Mg dendrite form was found in tensile fracture of as-cast MgAlCa-0.1Gd alloy, some tearing ridges occupied the fracture surface. Fig. 6c and d present the tensile fracture surfaces of hot rolled specimens with 80% deformation degree. The tear edge accompanied with dimples were found in hot rolled Mg-2.5Al₂Ca alloy, while only dimples were observed in hot rolled Mg-2.5Al₂Ca-0.1Al₈Mn₄Gd alloy. Therefore, it can be

concluded that addition of Gd into Mg–Al–Ca alloys facilitate the thermal deformation (such as hot rolling) and are conducive to improve their mechanical properties.

4. Conclusions

In this study, we proved that we could regulate the microstructure of Mg–Al–Ca magnesium alloy through the formation of Al₈Mn₄Gd phase. XRD and Bramfitt's theory indicates that spherical and dispersed Al₈Mn₄Gd phase firstly precipitate during the solidification process by introduction of Mn and Gd into Mg–Al–Ca magnesium alloy, Al₈Mn₄Gd phase could efficiently restricted the growth of dendritic α -Mg and disperse lamellar Al₂Ca in Mg-2.5Al₂Ca alloy. This is because that Al₈Mn₄Gd phase can serve as heterogeneous nucleation sites for the formation of α -Mg grains and Al₂Ca particles, especially for α -Mg. In addition, the introduction of Gd into Mg–Al–Ca alloys could also facilitate the hot rolling deformation. With 50% hot-roll deformation, the UTS and ductility of as-cast Mg-2.5Al₂Ca-0.1Al₈Mn₄Gd alloy were remarkably enhanced from 140 MPa and 1.1% to be 225 MPa and 1.6%. In contrast, the UTS and elongation of Mg-2.5Al₂Ca were only enhanced from 119 MPa and 0.95% to be 140 MPa and 1.1%.

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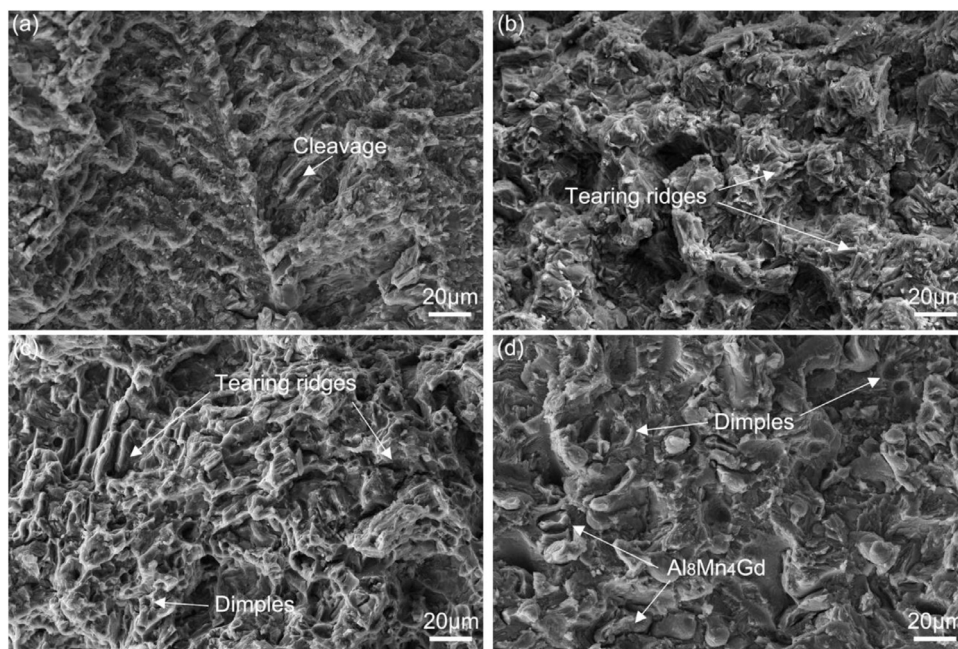


Fig.6. Fracture surface of specimens without hot roll treatment (a) and (b) and with hot rolled 80% degrees (c) and (d).

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